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(54) Title: ALKOXYLATED, QUATERNIZED DIAMINE DETERGENT INGREDIENTS

(57) Abstract

Quaternized alkylene diamines, and mixtures thereof, are used in detergent compositions.

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ALKOXYLATED, QUATERNIZED DIAMINE DETERGENT INGREDIENTS

TECHNICAL FIELD

The present invention relates to detergent compositions which comprise selected ingredients, including selected quaternized ethoxylated, alkylene diiamine compounds.

BACKGROUND OF THE INVENTION

The formulation of laundry detergents and other cleaning compositions presents a considerable challenge, since modern compositions are required to remove a variety of soils and stains from diverse substrates. Thus, laundry detergents, hard surface cleaners, shampoos and other personal cleansing compositions, hand dishwashing detergents and detergent compositions suitable for use in automatic dishwashers, and the like, all require the proper selection and combination of ingredients in order to function effectively. In general, such detergent compositions will contain one or more types of surfactants which are designed to loosen and remove certain soils and stains. However, while some detergent adjuncts and surfactants exhibit optimal performance on certain types of soils and stains, they can actually diminish performance on other soils. For example, surfactants which remove greasy/oily soils from fabrics can sometimes be sub-optimal for removing particulate soils. Moreover, the soils once removed from the substrate should be dispersed or suspended in the wash liquor to minimize redeposition on the substrate.

Thus, the efficient removal of particulate soils and the suspension of such soils can be problematic. Perhaps the most important particulate soils which pose these problems are the clay-type soils. Clay soil particles generally comprise negatively charged layers of aluminosilicates and positively charged cations (e.g. calcium) which are positioned between and hold together the negatively charged layers.

A variety of models can be proposed for compounds which would have clay soil removal properties. One model requires that the compound have two distinct characteristics. The first is the ability of the compound to adsorb onto the negatively charged layers of the clay particle. The second is the ability of the compound, once adsorbed, to push apart (swell) the negatively charged layers so that the clay particle loses its cohesive force and can be removed in the wash water.

In addition to clay soil removal, there is a need to keep the removed soil in suspension during the laundering cycle. Soil which is removed from the fabric and suspended in the wash water can redeposit on the surface of the fabric. This redeposited soil causes a dulling or "greying" effect which is especially noticeable on white fabrics.

To minimise this problem, anti-redeposition agents can be included in the detergent composition. For example EP-B-111 965 disclose the use in detergents of cationic compounds, which have both clay-soil removal and anti-redeposition properties.

Without being limited by theory, a model proposed for the anti-redeposition action of the positively charged anti-redeposition compounds is as follows. Adsorption of the positively charged molecule on the surface of clay particles in the wash water gives the particles the dispersancy properties of the molecule. As more and more of these compounds adsorb onto the suspended clay soil particles, the latter become encased within a hydrophilic layer. As such, the hydrophilically encased soil is prevented from redepositing on fabrics, in particular hydrophobic fabrics such as polyester, during the laundering cycle.

A considerable amount of research has been undertaken to find compounds which will effectively remove soils and prevent their redeposition. Thus, while a review of the literature would seem to indicate that a wide selection of surfactants and other components is available to the detergent manufacturer, the reality is that many such ingredients are specialty chemicals which are not suitable in low unit cost items such as home-use laundry detergents. Presumably due to economic considerations, the fact remains that most such home-use products such as laundry detergents still mainly comprise one or more of the conventional surfactants along with builders and conventional adjuncts. The need remains to formulate compositions with additional adjuncts which function reasonably well with a variety of soils and stains and a variety of fabrics.

Accordingly, there is a continuing search for improvements in detergents, especially laundry and dishwashing detergents and hard surface cleaners. However, the challenge to the detergent manufacturer seeking improved performance has been increased by various factors. For example, some non-biodegradable ingredients have fallen into disfavor. Effective phosphate builders have been banned by legislation in many countries. Costs associated with certain classes of compounds have impacted their use. As a result, the manufacturer is somewhat more limited than the literature would suggest in the selection of effective, yet affordable, ingredients. Still, the consumer has come to expect high quality and high performance in such compositions even when conducting cleaning operations under sub-optimal conditions, e.g., laundering fabrics in cool or cold water.

The literature does suggest that various nitrogen-containing compounds would be useful in a variety of cleaning compositions. Such materials, typically in the form of amino-, amido-, or quaternary ammonium or imidazolinium compounds, are often

designed for specialty use. For example, various amino and quaternary ammonium surfactants have been suggested for use in shampoo compositions and are said to provide cosmetic benefits to hair. Other nitrogen-containing surfactants are used in some laundry detergents to provide a fabric softening and anti-static benefit. For the most part, however, the commercial use of such materials is rather limited.

It has now been discovered that certain alkoxylated quaternary diamine (AQD) compounds can be used in various detergent compositions to boost performance, especially on particulate soils and for suspension of soils in the wash liquor. Importantly, it has further been discovered that low levels of these AQD compounds provide superior cleaning performance when used in certain combinations with otherwise known or conventional ingredients. Thus, the present invention provides an improvement in cleaning performance without the need to develop new, expensive surfactant species.

Moreover, the AQD soil removal/dispersants used in the present manner provide substantial advantages to the formulator over other dispersants known heretofore. For example, the AQD dispersants herein are compatible with the preferred alkyl sulfate, alkyl ethoxylated sulfate, and amidopropylamine detersive surfactants. Moreover, the AQD dispersants are formulatable over a broad pH range from 5 to 12. The AQD dispersants are also compatible with various perfume ingredients, unlike other quats known in the art.

In addition to the foregoing advantages, the AQD dispersants herein appear to minimize or eliminate redeposition of fatty acids/oily materials present in an aqueous laundry liquor back onto fabrics which have been previously soiled with body soils. Accordingly, the AQD dispersants herein have now been found to prevent the redeposition of polar lipids from an aqueous laundry bath back onto fabrics from whence body soils have been removed through the laundering process. Stated otherwise, in a laundering liquor, the AQD dispersants herein remove such polar lipids and keep them suspended in the aqueous medium, rather than allowing them to redeposit onto the cleaned fabrics.

In addition to the foregoing qualities, the AQD dispersants herein are surprisingly compatible with the polyanionic materials such as polyacrylates and acrylate/maleate copolymers which are used to provide a builder and/or dispersant function with many conventional detersive surfactants. Moreover, it has surprisingly been found that the combination of the AQD dispersants herein with specific ethoxylated polyethyleneimines with a MW of less than about 5,000 provide synergistic cleaning benefits.

Other advantages for the AQD dispersant herein include their ability to enhance enzymatic cleaning and fabric care performance in a laundering liquor. While not intending to be limited by theory, it is speculated that enzymes may be partially denatured by conventional anionic surfactants. It is further speculated that the AQD dispersants herein somehow interact with the anionic surfactants to inhibit that degradation. An alternate theory would suggest that, even when enzymes are used to degrade soils and stains, the degraded residues must be removed from the fabric surface. It may be speculated that the improved suspension of soil performance embodied in the AQD dispersants herein simply does a better job in removing these residues from the wash liquor and fabric surface.

In addition to the foregoing advantages, the AQD dispersants herein provide substantial cleaning enhancement with respect to clay soil removal from fabrics, as compared with conventional detergent mixtures. Again, while not intending to be limited by theory, it may be speculated that conventional cationic surfactants associate with the clay in "close-packed" fashion and render the clay more difficult to remove. In contrast, the alkoxylated AQD dispersants are believed to provide more open associations with clays, which are then more readily removed from fabric surfaces. Whatever the reason, the compositions herein containing the AQD dispersants provide improved performance over conventional dispersants with special regard to clay soil removal.

Still further advantages for the AQD dispersants herein have been discovered. For example, in bleaching compositions which comprise a bleach activator (as disclosed herein) it appears that some sort of ion pair or other associative complex is formed with the per-acid released from the activator. It may be speculated that this ion pair is carried more efficiently into the soil as a new, more hydrophobic agent, thereby enhancing bleach performance associated with the use of bleach activators such as nonanoyloxy benzene sulfonate (NOBS), tetraacetylethylenediamine (TAED), and peracids. Quite low levels of AQD dispersants gives rise to these results.

Moreover, in compositions without bleach, the formulator my choose to use somewhat higher levels of AQD dispersants to provide enhanced performance benefits. These benefits may be associated with the ability of the AQD dispersants herein to modify the solution characteristics of conventional anionic surfactants such as alkyl sulfates or alkyl ethoxylated sulfates to allow more of the surfactants to be available to perform their cleaning function. This is particularly true in situations faced by the formulator where the detergent composition is "underbuilt" with respect to calcium and/or magnesium water hardness ions

Mixtures of AQD dispersants can be blended and used to provide a broad spectrum of cleaning performance over a wide variety of soils and stains and under a wide range of usage conditions. Representative, but non-limiting, examples of such combinations of AQD dispersants are disclosed in the Examples hereinafter.

Various other advantages of the AQD dispersants over other dispersants known in the art are described in more detail hereinafter. As will be seen from the disclosures herein, the AQD dispersants, used in the manner of the present invention, successfully address many of the problems associated with the formulation of modern, high-performance detergent compositions. In particular, these dispersants allow the formulation of effective laundry compositions which can be used to remove a wide variety of soils and stains under a wide spectrum of usage conditions.

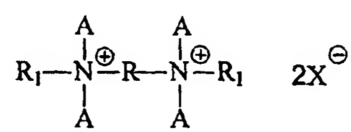
These and other advantages of the present invention will be seen from the following disclosures.

BACKGROUND ART

US 4,659,802 and US 4,664,848 describe cationic (quaternized) amine compounds which have clay-soil removal and anti-redeposition properties.

SUMMARY OF THE INVENTION

The present invention relates to cleaning compositions comprising or prepared by combining an effective amount of certain alkoxylated (especially ethoxylated) quaternary polyamine dispersants and one or more detersive (including fabric care) adjuncts, as disclosed hereinafter. The alkoxylated quaternary diamine (AQD) dispersants used in the present invention are of the general formula:



where R is selected from linear or branched C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, $[(CH_2CH_2O)_qCH_2CH_2]$- and -$CH_2CH(OH)CH_2O$-$(CH_2CH_2O)_qCH_2CH(OH)CH_2]$- where q is from about 1 to about 100. Each R_1 is independently selected from C_1-C_4 alkyl, C_7-C_{12} alkylaryl, or A. A is of the formula:

$$\underset{\displaystyle R_3}{\underset{|}{(CH}}\text{-}CH_2\text{-}O)_nB$$

where R_3 is selected from H or C_1-C_3 alkyl, n is from about 5 to about 100 and B is selected from H, C_1-C_4 alkyl, acetyl, or benzoyl; X is a water soluble anion

In preferred embodiments, R is selected from C_4 to C_8 alkylene, R_1 is selected from C_1-C_2 alkyl or C_2-C_3 hydroxyalkyl, and A is:

$$\underset{\displaystyle R_3}{\underset{|}{(CH}}\text{-}CH_2\text{-}O)_nH$$

where R_3 is selected from H or methyl, and n is from about 10 to about 50.

In another preferred embodiment R is linear or branched C_6, R_1 is methyl, R_3 is H, and n is from about 20 to about 50.

AQD's can be synthesized following the methods outline in US. Patent No. 4,664,848, or other ways known to those skilled in the art.

The levels of the AQD dispersants used to prepare finished laundry detergent compositions can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight.

The present invention encompasses the use of the aforesaid AQD dispersants to enhance the overall cleaning performance of detergent compositions which contain otherwise known ingredients. It has now been discovered that the overall cleaning performance of such detergent compositions can be improved by the incorporation of relatively small quantities of the AQD dispersants. Surprisingly, laundry cleaning performance with respect not only to greasy soils, but also body soil, builder sensitive soil, bleach sensitive soil, as well as food stains and sock soil is enhanced. Of course, the usage levels and mode of use of the AQD dispersants in detergent formulations of various types will depend on the desires of the formulator. Representative, but non-limiting, examples of such formulations include the following.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a specific surfactants, including alkyl sulfate (AS) and alkyl alkoxylated, especially ethoxylated, sulfates (AES). In other preferred embodiments, the compositions with AQD dispersants and these surfactants are substantially free of (i.e., have less than 5%, preferably less than 1%) of linear alkyl benzene sulfonate (LAS). In yet other embodiment, in nonaqueous liquid detergent compositions, the AQD is combined with linear alkyl benzene sulfonate.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and selected amine surfactants, such as amidopropyldimethylamines.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a polyester or oligoester soil release agent, especially a non-cotton soil release polymer or agent.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a polyethoxyated polyethyleneamine polymers or ethoxylated polyethyleneimine (PEI) polymers with a molecular weight of less than about 5,000, preferably less than about 2,000, more preferably from about 600 to about 1,000.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and an amylase or lipase enzyme, or mixtures thereof.

In yet other embodiments, examples of such formulations include the following:

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and chelants, especially ethylenediaminedisuccinate (EDDS) chelant.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a cellulase or protease enzyme, or mixtures thereof.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and an alkyl polyglycoside or polyhydroxy fatty acid amide surfactant.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a non-aqueous liquid carrier matrix.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a detergent granule having a bulk density of 650 g/L, or greater.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a source of magnesium ions, calcium ions, or mixtures thereof.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a dye-transfer inhibitor.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a manganese, cobalt or iron bleach catalyst.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a zeolite P or "MAP" builder.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a Mineral Builder.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and an oxygen bleach such as percarbonate bleach.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and one or more bleach activators.

Detergent compositions which comprise conventional detersive ingredients, an AQD dispersant and a photobleach.

The AQD dispersants used in the manner of the present invention also provide an improved method for removing and suspending the following soils and stains from fabrics: greasy food stain; particulate stain; body soils (including fabric "dinginess" caused by small, but noticeable, stain/soil accumulations over time) and other stains noted herein. Such stains and soils are removed from fabrics such as cotton, polyester/cotton blends (P/C) and double-knit polyester (DKPE). The method comprises contacting fabrics in need of removal of such soils with an effective amount of the compositions herein, in the presence of water, and preferably with agitation. Various suitable usage levels and methods are disclosed hereinafter.

With special regard to a fabric laundering context, the AQD compounds herein have the advantage that they are commercially available and are compatible with the various detersive ingredients such as builders, detersive enzymes, and the like, which are used in many modern, high quality, fully-formulated laundry detergents. Moreover, the AQD compounds exhibit satisfactory stability in the presence of the bleach ingredients commonly used in laundry detergent-plus-bleach compositions. Importantly, the AQD dispersants herein exhibit superior performance with respect to the removal of body soils and everyday soils such as sock soil. In short, the compositions herein provide improved performance for cleaning a broad spectrum of soils and stains including body soils from collars and cuffs, greasy soils, and enzyme/bleach sensitive stains such as spinach and coffee. The compositions herein also provide excellent cleaning on builder sensitive stains such as clay, and thus are especially useful in a nil-P context.

Moreover, the AQD dispersants herein provide improved fabric cleaning performance in the presence of bleach. This improvement in cleaning is seen at usage levels as low as 3 parts per million (ppm) of the AQD in the laundry liquor and is believed to be associated with increased perhydrolysis.

In addition, the AQD dispersants herein provide improved (even synergistic) performance with amylase, especially Duramyl®, and lipase, especially Lipolase Ultra®, enzymes. This improvement is seen especially in the absence of bleach.

All percentages, ratios and proportions herein are by weight of ingredients used to prepare the finished compositions unless otherwise specified. All documents cited herein are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

In one of its several aspects, this invention provides a means for enhancing the removal of greasy/oily soils by combining a lipase enzyme with an AQD dispersant. Greasy/oily "everyday "soils are a mixture of triglycerides, lipids, complex polysaccharides, inorganic salts and proteinaceous matter. When soiled garments are

stored before washing, some triglycerides are converted by bacterial action to fatty acids; lipase enzymes can be used to convert any remaining triglycerides to fatty acids through-the-wash. Generally, for formulas relying on hardness control by diffusion builders (e.g., layered silicates) pseudo unbuilt conditions will be present early a the wash which features a large intake of cold water. In these first minutes, fatty acids in the soil interact with the unbuilt hardness to form insoluble calcium lime-soaps which then hinder subsequent soil removal and cause soil residues to remain on the fabric after the wash. In unbuilt formulations this greasy/oily stain insolubilization will cause even more of a problem. Upon successive wearing/washing, residues build-up, leading to yellowing and entrapment of particulate dirt. Eventually, garments become dingy, are perceived as unwearable and are often discarded.

It has now been found that detergent compositions containing AQD dispersants and lipase enzyme deliver superior cleaning and whiteness performance vs. products containing either technology alone. Suitable lipase enzymes include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Further suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades). Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from Humicola lanuginosa as described in US Serial No. 08/341,826. (See also patent application WO 92/05249 viz. wherein the native lipase ex Humicola lanuginosa aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.) Preferably the Humicola lanuginosa strain DSM 4106 is used.

In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for fabric washing products. It is available from Novo Nordisk under the tradename Lipolase™, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor.

Lipase enzyme is incorporated into the composition in accordance with the invention at a level of from 50 LU to 8500 LU per liter wash solution. Preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

<u>Amylase</u> - Complete removal of the very hydrophobic "everyday" or "body" soils is difficult and low levels of residual soils often remain on the fabric after washing. These residues build up and act like an amorphous glue between the fibers, entrapping particulate dirt and leading to fabric yellowing. It has now further been discovered that detergent compositions containing a combination of the water-soluble AQD dispersants herein and amylase enzymes delivers superior cleaning and whiteness performance vs. compositions containing either technology alone.

Such amylase enzymes include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. These enzymes are incorporated into detergent compositions at a level from 0.00018% to 0.060% pure enzyme by weight of the total composition, more preferably from 0.00024% to 0.048% pure enzyme by weight of total weight composition.

Specific amylase enzymes for use in the detergent compositions of the present invention therefore include :

(a) α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Such Phadebas® α-amylase activity assay is described at pages 9-10, WO95/26397.

(b) α-amylases according (a) comprising the amino sequence shown in the SEQ ID listings in the above cited reference. or an α-amylase being at least 80% homologous with the amino acid sequence shown in the SEQ ID listing.

(c) α-amylases according (a) comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp.

A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%

(d) α-amylases according (a-c) wherein the α-amylase is obtainable from an alkalophilic Bacillus species; and in particular, from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935.

In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a Bacillus strain byt also an amylase encoded by a DNA sequence isolated from such a Bacillus strain and produced in an host organism transformed with said DNA sequence.

(e)α-amylase showing positive immunological cross-reactivity with antibodies raised against an α-amylase having an amino acid sequence corresponding respectively to those α-amylases in (a-d).

(f) Variants of the following parent α-amylases which (i) have one of the amino acid sequences shown in corresponding respectively to those α-amylases in (a-e), or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an α-amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence wich hybridizes with the same probe as a DNA sequence encoding an α-amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent α-amylase has been deleted; and/or

2.at least one amino acid residue of said parent α-amylase has been replaced by a different amino acid residue; and/or

3. at least one amino acid residue has been inserted relative to said parent α-amylase;
said variant having an α-amylase activity and exhibiting at least one of the following properties relative to said parent α-amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or α-amylolytic activity at neutral to relatively high pH values, increased α-amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α-amylase variant to the pH of the medium.

Said variants are described in the patent application PCT/DK96/00056.

Other amylases suitable herein include, for example, α-amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents such as automatic dishwashing types, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens, B. subtilis,* or *B.*

stearothermophilus; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Alkyl alkoxylated sulfates and/or alkyl sulfates - The alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, more preferably C_{12}-C_{15} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include ethanol-, triethanol-, methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{15} alkyl polyethoxylate (1.0) sulfate (C_{12}-$C_{15}E(1.0)M$), C_{12}-C_{15} alkyl polyethoxylate (2.25) sulfate (C_{12}-$C_{15}E(2.25)M$), C_{12}-C_{15} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{15}E(3.0)M$), and C_{12}-C_{15} alkyl polyethoxylate (4.0) sulfate (C_{12}-$C_{15}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

The alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_8-C_{18} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{18} alkyl component, more preferably a C_{12}-C_{15} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Commerical alkyl alkoxylate sulfates comprise a mixture of compounds with varying degrees of alkoxylation. For example, C_{12-15} polyoxyethylene (3) sulfate from Shell Chemical Company, Houston, TX, will contain molecules with from zero ethoxylates to five or more, for an average degree of ethoxylation = 3. The lower the average degree of ethoxylation of a given sample, the higher the level of alkyl sulfate (EO=0) which may be present in the mixture.

For purposes of this invention, the total amount of alkyl sulfate present in the detergent compositions herein include not only the alkyl sulfate added to the composition but also any alkyl sulfate which may be present in the alkyl alkoxyate sulfate surfactant mixture.

In another embodiment of the invention herein, surprisingly it has been found that in liquid detergents, the benefits associated with the AQD dispersant, and its combination with ethoxylated polyethyleneimines (PEI), are greatly enhanced when the surfactant system of the detergent comprises sodium alkylethoxysulfate (AES) and nil alkyl sulfate and alkylbenzenesulfonate. By "nil" is meant less than 5%, preferably less than 1%.

In yet another embodiment of the invention herein, surprisingly is has been found that in non-aqueous liquid detergents, the benefits associated with the AQD dispersant are enhanced when the surfactant system of the detergent comprises linear alkylbenzenesulfonate.

<u>The amine</u> - Suitable amine surfactants for use herein include amines according to the formula:

$$R_1\text{-}X\text{-}(CH_2)_n\text{-}N\begin{matrix} R_3 \\ \\ R_4 \end{matrix}$$

wherein R_1 is a C_6-C_{12} alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R_3 and R_4 are

individually selected from H, C_1-C_4 alkyl, or (CH_2-CH_2-O(R_5)) wherein R_5 is H or methyl.

Preferred amines include the following:

$$R_1\text{-}(CH_2)_2\text{-}NH_2$$

$$R_1\text{-}O\text{-}(CH_2)_3\text{-}NH_2$$

$$R_1\text{-}C(O)\text{-}NH\text{-}(CH_2)_3\text{-}N(CH_3)_2$$

$$R_1\text{-}N\begin{matrix} CH_2\text{-}CH(OH)\text{-}R_5 \\ CH_2\text{-}CH(OH)\text{-}R_5 \end{matrix}$$

wherein R_1 is a C_6-C_{12} alkyl group and R_5 is H or CH_3.

In a highly preferred embodiment, the amine is described by the formula:

$$R_1\text{-}C(O)\text{-}NH\text{-}(CH_2)_3\text{-}N(CH_3)_2$$

wherein R_1 is C_8-C_{12} alkyl.

Particularly preferred amines include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C_8-C_{12} bis(hydroxyethyl)amine, C_8-C_{12} bis(hydroxyisopropyl)amine, and C_8-C_{12} amido-propyl dimethyl amine, and mixtures.

This invention also provides detergent compositions which deliver effective cleaning of greasy/oily everyday soils via use of percarbonate bleach with an AQD dispersants as disclosed herein. Percarbonate, which delivers peroxide bleach into the wash, is a cornerstone technology of modern, ultra-compact granular laundry detergent formulas. Peroxide bleach is very hydrophilic and, while it cannot match the bleaching effectiveness delivered by peracids (formed for example from peroxide interaction with TAED), it is effective at decoloration of pigments (e.g., in particulates or beverage stains) and also can help remove the color from the organic residues associated with body soils. Unexpectedly, it has now been discovered that compositions containing AQD dispersants and percarbonate bleach deliver superior cleaning and whiteness performance.

This invention also provides detergent compositions which deliver effective cleaning of greasy/oily everyday soils by means of hydrophobic bleach activators used in combination with a water-soluble AQD dispersant of the present type. Everyday soil cleaning and whiteness benefits for hydrophobic bleach activators and peracids have

already been demonstrated. Such materials are, to a limited degree, able to penetrate complex/greasy oily soils. It has now been found that detergent and bleach compositions containing AQD and hydrophobic bleach activators (including preformed peracids) deliver superior cleaning and whiteness performance.

This invention also provides detergent compositions which deliver effective cleaning of greasy/oily "everyday" soils (and accidental soils), via use of polyethoxyated-polyamine polymers (PPP) with the AQD dispersants herein. As noted, greasy/oily "everyday" soils (e.g., on collars, pillowcases) are a mixture of triglycerides, lipids, complex polysaccharides, inorganic salts and proteinaceous matter. Complete removal of these very hydrophobic soils is difficult and low levels of residual stain often remain on the fabric after washing. To improve performance in this key area, various soil dispersant polymers have been developed. Characteristic features of these materials include: (1) a reasonably low molecular weight "hydrophobic" polyamine backbone (which is slightly cationic in nature providing an affinity for soils and fabrics); and (2) pendant "hydrophilic" polyethoxylate groups which provide steric stabilization and greasy soil suspension. During the wash, these polymers work at the stain/wash liquor interface.

Surprisingly, it has now been discovered that detergent compositions containing the AQD dispersants herein and polyethoxylated-polyamine polymers deliver superior cleaning and whiteness performance vs. compositions containing either technology alone. Benefits for the mixed system are believed to be the result of: (1) AQD action on the stain surface to prevent lime soap formation and to lift off any calcium soaps present, thereby facilitating improved polymer deposition; (2) AQD providing solubilization deep into the soil, while the polymer acts as a "grease removal shuttle", stripping out the AQD-solubilized stain components and dispersing them into the wash liquor.

The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See

U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C_2 alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:

$$[H_2NCH_2CH_2]_n-[\overset{H}{\overset{|}{N}}CH_2CH_2]_m-[\overset{|}{N}CH_2CH_2]_n-NH_2$$

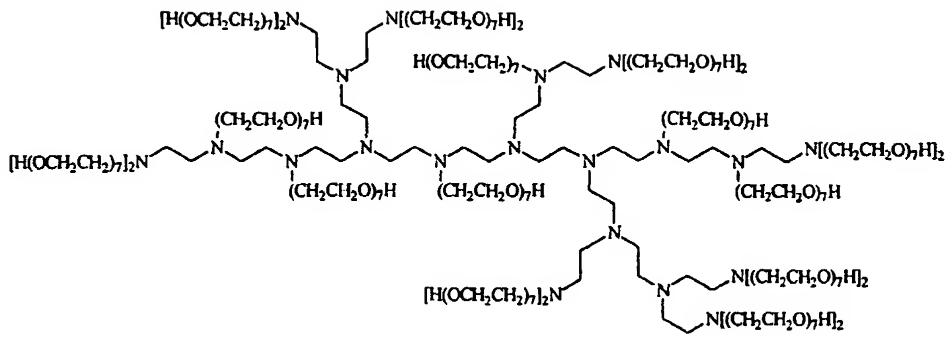
wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Examples of modified cotton soil release polymers of the present invention comprising PEI's, are illustrated in Formulas I - IV:

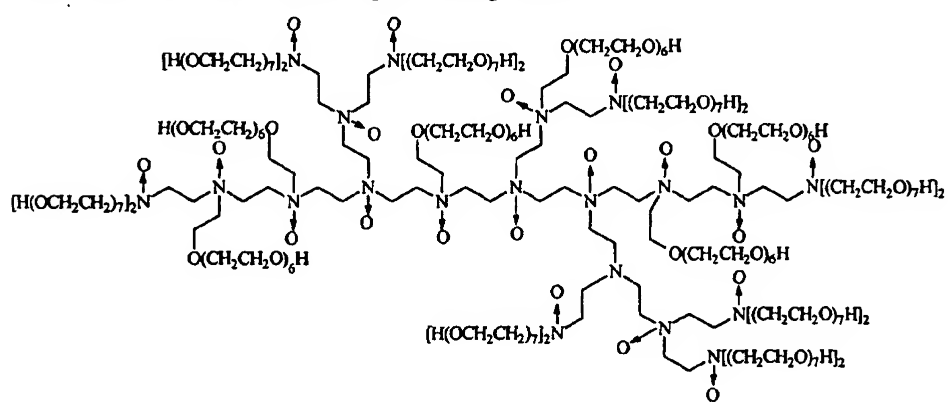
Formula I depicts a cotton soil release polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, having the formula



Formula I

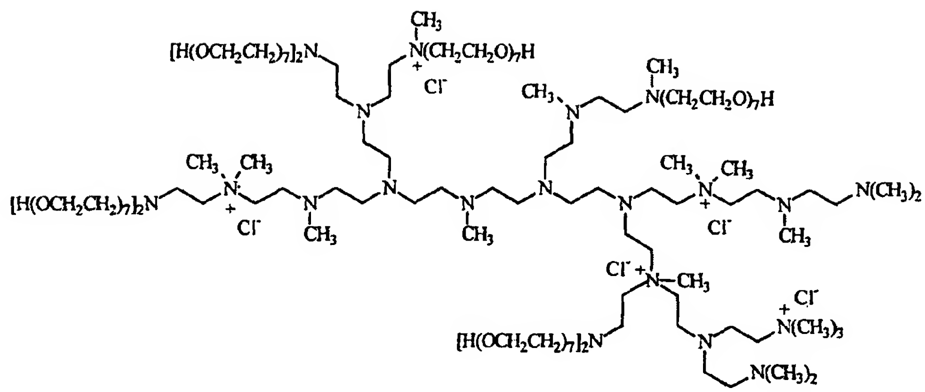
This is an example of a cotton soil release polymer that is fully modified by one type of moiety.

Formula II depicts a cotton soil release polymer comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said cotton soil release agent having the formula



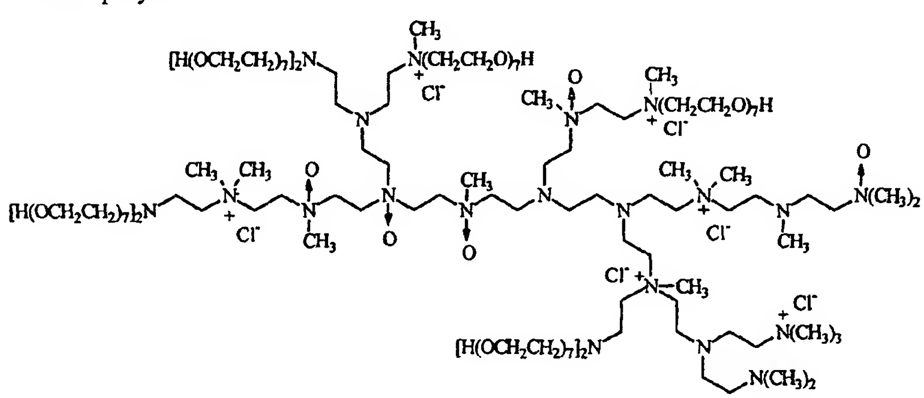
Formula II

Formula III depicts a cotton soil release polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(CH_2CH_2O)_7H$, or methyl groups. The modified PEI cotton soil release polymer has the formula



Formula III

Formula IV depicts a cotton soil release polymer comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(CH_2CH_2O)_7H$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting cotton soil release polymer has the formula



Formula IV

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

The present invention employs an "effective amount" of the AQD dispersant to improve the performance of cleaning compositions which contain other adjunct ingredients. By an "effective amount" of the AQD dispersants and adjunct ingredients herein is meant an amount which is sufficient to improve, either directionally or significantly at the 90% confidence level, the performance of the cleaning composition against at least some of the target soils and stains. Thus, in a composition whose targets include certain food stains, the formulator will use sufficient AQD to at least directionally improve cleaning performance against such stains. Likewise, in a composition whose targets include clay soil, the formulator will use sufficient AQD to at least directionally improve cleaning performance against such soil. Importantly, in a fully-formulated laundry detergent the AQD dispersants can be used at levels which provide at least a directional improvement in cleaning performance over a wide variety of soils and stains, as will be seen from the data presented hereinafter.

As noted, the AQD dispersants are used herein in detergent compositions in combination with detersive surfactants at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a fabric laundry composition, such "usage levels" can vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water and the type of washing machine.

As can be seen from the foregoing, the amount of AQD dispersant used in a machine-wash laundering context can vary, depending on the habits and practices of the user, the type of washing machine, and the like. In this context, however, one heretofore unappreciated advantage of the AQD dispersants is their ability to provide at least directional improvements in performance over a spectrum of soils and stains.

Various other cleaning compositions can also be formulated using an effective amount of the AQD dispersants in the manner of this invention. Such compositions include, but are not limited to, hand dishwashing products (especially liquids or gels), hard surface cleaners, shampoos, personal cleansing bars, laundry bars, and the like. Since the habits and practices of the users of such compositions show minimal variation, it is satisfactory to include from about 0.25% to about 5%, preferably from about 0.45% to about 2%, by weight, of the AQD dispersants in such compositions.

<u>Detersive Surfactants</u> - Nonlimiting examples of anionic surfactants useful herein typically at levels from about 1% to about 55%, by weight, primary, branched-chain and random C_{10}-C_{20} alkyl sulfates ("AS"), the C_{10}-C_{18} secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^-M^+)\ CH_3$ and $CH_3\ (CH_2)_y(CHOSO_3^-M^+)\ CH_2CH_3$ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a

water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C_{10}-C_{18} alpha-sulfonated fatty acid esters, the C_{10}-C_{18} sulfated alkyl polyglycosides, the C_{10}-C_{18} alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), and C_{10}-C_{18} alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates). The C_{12}-C_{18} betaines and sulfobetaines ("sultaines"), C_{10}-C_{18} amine oxides, and the like, can also be included in the overall compositions. C_{10}-C_{20} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10}-C_{16} soaps may be used. Other conventional useful surfactants are listed in standard texts.

Preferably the compositions of the invention are substantiall free of C_{11}-C_{18} alkyl benzene sulfonates ("LAS").

Nonionic Surfactants - Nonlimiting examples of nonionic surfactants useful herein typically at levels from about 1% to about 55%, by weight include the alkoxylated alcohols (AE's) and alkyl phenols, polyhydroxy fatty acid amides (PFAA's), alkyl polyglycosides (APG's), C_{10}-C_{18} glycerol ethers, and the like.

More specifically, the condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide (AE) are suitable for use as the nonionic surfactant in the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 1 to about 10 moles, preferably 2 to 7, most preferably 2 to 5, of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include: Tergitol™ 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide) and Tergitol™ 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-3 (the condensation product of C_{12}-C_{13} linear alcohol with 3 moles of ethylene oxide), Neodol ™ 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide) and Neodol™ 45-5 (the condensation product of C_{14}-C_{15} linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company; Kyro™ EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company; and Genapol LA O3O or O5O (the condensation product of C_{12}-C_{14} alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst.

The preferred range of HLB in these AE nonionic surfactants is from 8-11 and most preferred from 8-10. Condensates with propylene oxide and butylene oxides may also be used.

Another class of preferred nonionic surfactants for use herein are the polyhydroxy fatty acid amide surfactants of the formula.

$$R_2\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{R^1}{|}}{N}\text{—}Z,$$

wherein R^1 is H, or C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or C_{15-17} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction. Typical examples include the C_{12}-C_{18} and C_{12}-C_{14} N-methylglucamides. See U.S. 5,194,639 and 5,298,636. N-alkoxy polyhydroxy fatty acid amides can also be used; see U.S. 5,489,393.

Also useful as the nonionic surfactant in the present invention are the alkylpolysaccharides such as those disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms, and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.
The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10,

preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are also suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal^{TM} CO-630, marketed by the GAF Corporation; and Triton^{TM} X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant in the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic^{TM} surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene

oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic^{TM} compounds, marketed by BASF.

The following illustrates various other adjunct ingredients which may be used in the compositions of this invention, but is not intended to be limiting thereof. While the combination of the AQD with such adjunct compositional ingredients can be provided as finished products in the form of liquids, gels, bars, or the like using conventional techniques, the manufacture of the granular laundry detergents herein requires some special processing techniques in order to achieve optimal performance. Accordingly, the manufacture of laundry granules will be described hereinafter separately in the Granules Manufacture section (below), for the convenience of the formulator.

Builders - Detergent builders can optionally but preferably be included in the compositions herein, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal of particulate soils from surfaces. Builders can operate via a variety of mechanisms including forming soluble or insoluble complexes with hardness ions, by ion exchange, and by offering a surface more favorable to the precipitation of hardness ions than are the surfaces of articles to be cleaned. Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at least about 1% builder. Liquid formulations typically comprise about 5% to about 50%, more typically 5% to 35% of builder. Granular formulations typically comprise from about 10% to about 80%, more typically 15% to 50% builder by weight of the detergent composition. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional-structure as well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates,

especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing detergent compositions.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein. In terms of relative quantities of surfactant and builder in the present detergents, preferred builder systems are typically formulated at a weight ratio of surfactant to builder of from about 60:1 to about 1:80. Certain preferred laundry detergents have said ratio in the range 0.90:1.0 to 4.0:1.0, more preferably from 0.95:1.0 to 3.0:1.0.

P-containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

Suitable silicate builders include alkali metal silicates, particularly those liquids and solids having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1, including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL®, e.g., BRITESIL H2O; and layered silicates, e.g., those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. NaSKS-6, sometimes abbreviated "SKS-6", is a crystalline layered aluminium-free δ-Na_2SiO_5 morphology silicate marketed by Hoechst and is preferred especially in granular laundry compositions. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043. Other layered silicates, such as those having the general formula $NaMSi_xO_{2x+1}\cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0, can also or alternately be used herein. Layered silicates from Hoechst also include NaSKS-5, NaSKS-7 and NaSKS-11, as the α, β and γ layer-silicate forms. Other silicates may also be useful, such as magnesium silicate, which can serve as a crispening agent in granules, as a stabilising agent for bleaches, and as a component of suds control systems.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof having chain structure and a composition represented by the following general formula in an anhydride form: $xM_2O\cdot ySiO_2.zM'O$ wherein M is Na and/or K, M' is Ca and/or Mg; y/x is 0.5 to 2.0 and z/x is 0.005 to 1.0 as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973,

although sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, and other carbonate minerals such as trona or any convenient multiple salts of sodium carbonate and calcium carbonate such as those having the composition $2Na_2CO_3.CaCO_3$ when anhydrous, and even calcium carbonates including calcite, aragonite and vaterite, especially forms having high surface areas relative to compact calcite may be useful, for example as seeds or for use in synthetic detergent bars.

Aluminosilicate builders are especially useful in granular detergents, but can also be incorporated in liquids, pastes or gels. Suitable for the present purposes are those having empirical formula: $[M_z(AlO_2)_z(SiO_2)_v]\cdot xH_2O$ wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP. Natural types, including clinoptilolite, may be used. Zeolite A has the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$ wherein x is from 20 to 30, especially 27. Dehydrated zeolites ($x = 0$ - 10) may also be used. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrates, e.g., citric acid and soluble salts thereof are important carboxylate builders e.g., for heavy duty liquid detergents, due to availability from renewable resources and biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicates. Oxydisuccinates are also especially useful in such compositions and combinations.

Where permitted, and especially in the formulation of bars used for hand-laundering operations, alkali metal phosphates such as sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates, e.g., those of U.S. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137 can also be used and may have desirable antiscaling properties.

Certain detersive surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as detersive surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 1967. See also Diehl, U.S. 3,723,322.

Other types of inorganic builder materials which can be used have the formula $(M_x)_i\ Ca_y\ (CO_3)_z$ wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25, M_i are cations, at least one of which is a water-soluble, and the equation $\Sigma_{i\,=\,1\text{-}15}(x_i$ multiplied by the valence of $M_i) + 2y = 2z$ is satisfied such that the formula has a neutral or "balanced" charge. These builders are referred to herein as "Mineral Builders". Waters of hydration or anions other than carbonate may be added provided that the overall charge is balanced or neutral. The charge or valence effects of such anions should be added to the right side of the above equation. Preferably, there is present a water-soluble cation selected from the group consisting of hydrogen, water-soluble metals, hydrogen, boron, ammonium, silicon, and mixtures thereof, more

preferably, sodium, potassium, hydrogen, lithium, ammonium and mixtures thereof, sodium and potassium being highly preferred. Nonlimiting examples of noncarbonate anions include those selected from the group consisting of chloride, sulfate, fluoride, oxygen, hydroxide, silicon dioxide, chromate, nitrate, borate and mixtures thereof. Preferred builders of this type in their simplest forms are selected from the group consisting of $Na_2Ca(CO_3)_2$, $K_2Ca(CO_3)_2$, $Na_2Ca_2(CO_3)_3$, $NaKCa(CO_3)_2$, $NaKCa_2(CO_3)_3$, $K_2Ca_2(CO_3)_3$, and combinations thereof. An especially preferred material for the builder described herein is $Na_2Ca(CO_3)_2$ in any of its crystalline modifications. Suitable builders of the above-defined type are further illustrated by, and include, the natural or synthetic forms of any one or combinations of the following minerals: Afghanite, Andersonite, AshcroftineY, Beyerite, Borcarite, Burbankite, Butschliite, Cancrinite, Carbocernaite, Carletonite, Davyne, DonnayiteY, Fairchildite, Ferrisurite, Franzinite, Gaudefroyite, Gaylussite, Girvasite, Gregoryite, Jouravskite, KamphaugiteY, Kettnerite, Khanneshite, LepersonniteGd, Liottite, MckelveyiteY, Microsommite, Mroseite, Natrofairchildite, Nyerereite, RemonditeCe, Sacrofanite, Schrockingerite, Shortite, Surite, Tunisite, Tuscanite, Tyrolite, Vishnevite, and Zemkorite. Preferred mineral forms include Nyererite, Fairchildite and Shortite.

Enzymes - Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition. Preferred detersive enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though more and more bleach compatible though successive improvements, have a remaining degree of bleach deactivation susceptibility.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents, such as in automatic dishwashing, it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble . When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to

position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME®(Novo) are especially useful. See also WO 9117243 to Novo.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Enzyme Stabilizing System - The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions, for example automatic dishwashing compositions, may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent

chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during dish- or fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski et al.

Polymeric Soil Release Agent - Known polymeric soil release agents, hereinafter "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with SRA to be more easily cleaned in later washing procedures.

SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without of course forming a densely crosslinked overall structure.

Suitable SRA's include: a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink: such ester oligomers can be prepared by (a) ethoxylating allyl alcohol, (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/ oligomerization procedure and (c) reacting the product of (b) with sodium metabisulfite in water; the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al, for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"); the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al, the latter being

typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; and the C_1-C_4 alkylcelluloses and C_4 hydroxyalkyl celluloses; see U.S. 4,000,093, December 28, 1976 to Nicol, et al. Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C_1-C_6 vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 90-80% by weight of polyoxyethylene terephthalate, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

Another preferred SRA is an oligomer having empirical formula $(CAP)_2(EG/PG)_5(T)_5(SIP)_1$ which comprises terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propylene (EG/PG) units and which is preferably terminated with end-caps (CAP), preferably modified isethionates, as in an oligomer comprising one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a defined ratio, preferably about 0.5:1 to about 10:1, and two end-cap units derived from sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said SRA preferably further comprises from 0.5% to 20%, by weight of the oligomer, of a crystallinity-reducing stabiliser, for example an anionic surfactant such as linear sodium dodecylbenzenesulfonate or a member selected from xylene-, cumene-, and toluene-sulfonates or mixtures thereof, these stabilizers or modifiers being introduced into the synthesis pot, all as taught in U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na 2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na- dimethyl 5-sulfoisophthalate, EG and PG.

Yet another group of preferred SRA's are oligomeric esters comprising: (1) a backbone comprising (a) at least one unit selected from the group consisting of dihydroxysulfonates, polyhydroxy sulfonates, a unit which is at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, and

combinations thereof; (b) at least one unit which is a terephthaloyl moiety; and (c) at least one unsulfonated unit which is a 1,2-oxyalkyleneoxy moiety; and (2) one or more capping units selected from nonionic capping units, anionic capping units such as alkoxylated, preferably ethoxylated, isethionates, alkoxylated propanesulfonates, alkoxylated propanedisulfonates, alkoxylated phenolsulfonates, sulfoaroyl derivatives and mixtures thereof. Preferred of such esters are those of empirical formula:

{(CAP)x(EG/PG)y'(DEG)y"(PEG)y'"(T)z(SIP)z'(SEG)q(B)m}

wherein CAP, EG/PG, PEG, T and SIP are as defined hereinabove, (DEG) represents di(oxyethylene)oxy units; (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units; (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone; x is from about 1 to about 12; y' is from about 0.5 to about 25; y" is from 0 to about 12; y'" is from 0 to about 10; y'+y"+y'" totals from about 0.5 to about 25; z is from about 1.5 to about 25; z' is from 0 to about 12; z + z' totals from about 1.5 to about 25; q is from about 0.05 to about 12; m is from about 0.01 to about 10; and x, y', y", y'", z, z', q and m represent the average number of moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from about 500 to about 5,000.

Preferred SEG and CAP monomers for the above esters include Na-2-(2-,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-{2-(2-hydroxyethoxy) ethoxy} ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl alcohol. Preferred SRA esters in this class include the product of transesterifying and oligomerizing sodium 2-{2-(2-hydroxyethoxy)ethoxy}ethanesulfonate and/or sodium 2-[2-{2-(2-hydroxyethoxy)-ethoxy}ethoxy]ethanesulfonate, DMT, sodium 2-(2,3-dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)2(T)5(EG/PG)1.4(SEG)2.5(B)0.13 wherein CAP is (Na+ $^{-}O_3S[CH_2CH_2O]3.5$)- and B is a unit from glycerin and the mole ratio EG/PG is about 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

Additional classes of SRA's include (I) nonionic terephthalates using diisocyanate coupling agents to link up polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al; (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With a proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have

hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.; (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF made, by grafting acrylic monomers on to sulfonated polyesters; these SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie; (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate on to proteins such as caseins, see EP 457,205 A to BASF (1991); (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al, DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 4,240,918, 4,787,989, 4,525,524 and 4,877,896.

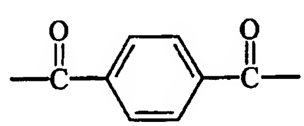
Non-cotton Soil Release Polymers

The non-cotton soil release polymers to be used in the laundry detergent compositions of the present invention are the following.

Preferred non-cotton soil release agent - A. Suitable for use in the laundry detergent compositions of the present invention are preferred non-cotton soil release polymers comprising:

a) a backbone comprising:

i) at least one moiety having the formula:



;

ii) at least one moiety having the formula:

$$-O-\underset{R^{10}}{\overset{R^{10}}{\underset{|}{\overset{|}{R^9}}}}-(O-\underset{R^{10}}{\overset{R^{10}}{\underset{|}{\overset{|}{R^9}}}})_i-O-$$

wherein R^9 is C_2-C_6 linear alkylene, C_3-C_6 branched alkylene, C_5-C_7 cyclic alkylene, and mixtures thereof; R^{10}

is independently selected from hydrogen or $-L-SO_3^-M^+$; wherein L is a side chain moiety selected from the group consisting of alkylene, oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxyalkyleneoxyarylene, poly(oxyalkylene)oxyarlyene, alkylenepoly(oxyalkylene),and mixtures thereof; M is hydrogen or a salt forming cation; i has the value of 0 or 1;

iii) at least one trifunctional, ester-forming, branching moiety;

iv) at least one 1,2-oxyalkyleneoxy moiety; and

b) one or more capping units comprising:

i) ethoxylated or propoxylated hydroxyethanesulfonate or ethoxylated or propoxylated hydroxypropanesulfonate units of the formula $(MO_3S)(CH_2)_m(R^{11}O)_n$-, where M is a salt forming cation such as sodium or tetralkylammonium, R^{11} is ethylene or propylene or a mixture thereof, m is 0 or 1, and n is from 1 to 20;

ii) sulfoaroyl units of the formula $-(O)C(C_6H_4)(SO_3^-M^+)$, wherein M is a salt forming cation;

iii) modified poly(oxyethylene)oxy monoalkyl ether units of the formula $R^{12}O(CH_2CH_2O)_k$-, wherein R^{12} contains from 1 to 4 carbon atoms and k is from about 3 to about 100; and

iv) ethoxylated or propoxylated phenolsulfonate end-capping units of the formula $MO_3S(C_6H_4)(OR^{13})_nO$-, wherein n is from 1 to 20; M is a salt-forming cation; and R^{13} is ethylene, propylene and mixtures thereof.

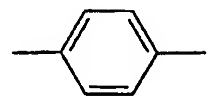
This type of preferred non-cotton soil release polymer of the present invention may be described as having the formula

$$[(Cap)(R^4)_t][(A-R^1-A-R^2)_u(A-R^1-A-R^3)_v(A-R^1-A-R^5)_w \\ -A-R^1-A-][(R^4)_t(Cap)]$$

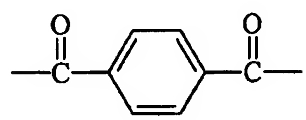
wherein A is a carboxy linking moiety having the formula

$$-\overset{\displaystyle O}{\overset{\|}{C}}-,$$

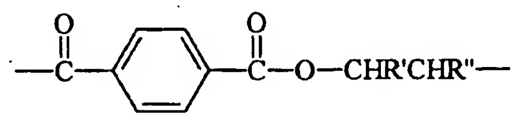
R^1 is arylene, preferably a 1,4-phenylene moiety having the formula



such that when A units and R^1 units are taken together in the formula A-R^1-A they form a terephthalate unit having the formula

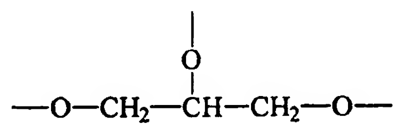


R^2 units are ethyleneoxy or 1,2-propyleneoxy. R^2 units are combined with terephthalate moieties to form (A-R^1-A-R^2) units having the formula

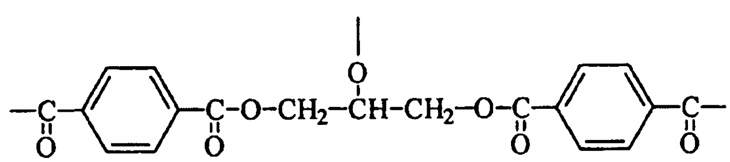


wherein R' and R" are either hydrogen or methyl provided that R' and R" are not both methyl at the same time.

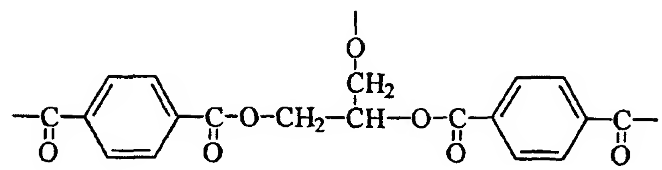
R^3 units are trifunctional, ester-forming, branching moieties having the formula



Preferably R^3 units comprise a glycerol moiety which is placed into the soil release polymer backbone to provide a branch point. When R^3 units are combined with terephthalate moieties to form units of the polymer backbone, for example, (A-R^1-A-R^3)-A-R^1-A units, these units have the formula

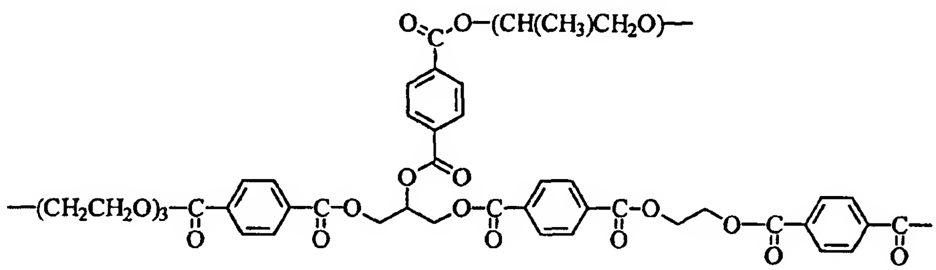


or the formula



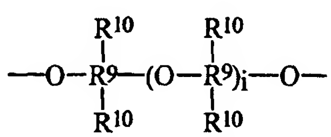
wherein one terephthalate residue is taken to be a part of the (A-R^1-A-R^3) unit while the second terephthalate comprises a part of another backbone unit, such as a (A-R^1-A-R^2) unit, a (A-R^1-A-R^5) unit, a -A-R^1-A-[$(R^4)_t$(Cap)] unit or a second (A-R^1-A-R^3) unit. The third functional group, which is the beginning of the branching chain, is also typically bonded to a terephthalate residue also a part of a (A-R^1-A-R^2) unit, a (A-R^1-A-R^5) unit, a -A-R^1-A-[$(R^4)_t$(Cap)] unit or another (A-R^1-A-R^3) unit.

An example of a section of a soil release polymer containing a "trifunctional, ester-forming, branching moiety" R^3 unit which comprises a glycerol unit, has the formula



R^4 units are R^2, R^3 or R^5 units.

R^5 units are units having the formula



wherein R^9 is C_2-C_6 linear alkylene, C_3-C_6 branched alkylene, and mixtures thereof; preferably R^{10} is independently selected from hydrogen or -L-$SO_3^-M^+$; wherein L is a side chain moiety selected from the group consisting of alkylene, oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxyalkyleneoxyarylene, poly(oxyalkylene)oxyarlyene, alkylenepoly(oxyalkylene),and mixtures thereof; M is hydrogen or a salt forming cation; i has the value of 0 or 1;

Each carbon atom of the R^9 units is substituted by R^{10} units that are independently selected from hydrogen or -L-$SO_3^-M^+$, provided no more than one -L-$SO_3^-M^+$ units is attached to an R^9 unit; L is a side chain connecting moiety selected

from the group consisting of alkylene, oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxyalkyleneoxyarylene, poly(oxyalkylene)oxyarlyene, alkylenepoly(oxyalkylene),and mixtures thereof.

M is a cationic moiety selected from the group consisting of lithium, sodium, potassium, calcium, and magnesium, preferably sodium and potassium.

Preferred R^5 moieties are essentially R^{10} substituted C_2-C_6 alkylene chains. The R^5 units comprise either one C_2-C_6 alkylene chain substituted by one or more independently selected R^{10} moieties (preferred) or two C_2-C_6 alkylene chains said alkylene chains joined by an ether oxygen linkage, each alkylene chain substituted by one or more independently selected R^{10} moieties, that is R^5 may comprise two separate R^9 units, each of which is substituted by one or more independently selected R^{10} moieties. Preferably only one carbon atom of each R^9 moiety is substituted by an $-L-SO_3^-M^+$ unit with the remaining R^{10} substituents comprising a hydrogen atom. When the value of the index i is equal to 1 (two R^9 units comprise the R^5 unit), a preferred formula is

$$-\mathrm{O}-\underset{R^{10}}{\overset{R^{10}}{\mathrm{C}}}-\underset{R^{10}}{\overset{R^{10}}{\mathrm{C}}}-\mathrm{O}-\underset{R^{10}}{\overset{R^{10}}{\mathrm{C}}}-\underset{R^{10}}{\overset{R^{10}}{\mathrm{C}}}-\mathrm{O}-$$

wherein each R^9 comprises a C_2 alkylene moiety. Preferably one R^{10} moiety is $-L-SO_3^-M^+$, preferably the C_2 carbon is substituted by the $-L-SO_3^-M^+$ moiety, and the balance are hydrogen atoms, having therefore a formula:

$$-\underset{CH_2(OCH_2CH_2)_xSO_3^-M^+}{\underset{|}{CH}}CH_2-O-CH_2CH_2-$$

wherein L is a polyethyleneoxymethyl substituent, x is from 0 to about 20.

As used herein, the term "R^5 moieties consist essentially of units

$$-\mathrm{O}-\underset{R^{10}}{\overset{R^{10}}{R^9}}-(\mathrm{O}-\underset{R^{10}}{\overset{R^{10}}{R^9}})_i-\mathrm{O}-$$

having the index i equal to 0 wherein R^{10} units are hydrogen and one R^{10} units is equal to $-L-SO_3^-M^+$, wherein L is a side chain connecting moiety selected from the group consisting of alkylene, alkenylene, alkoxyalkylene, oxyalkylene, arylene, alkylarylene, alkoxyarylene and mixtures thereof", refers to the preferred compounds of the present

invention wherein the R^{10} moieties consist of one $-L-SO_3^-M^+$ moiety and the rest of the R^{10} moieties are hydrogen atoms, for example a

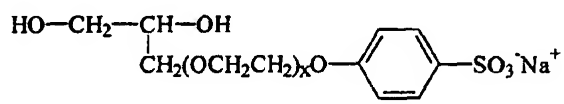
$$\begin{array}{l} -O-CH_2-CH-O- \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2(OCH_2CH_2)_xSO_3^-\,Na^+ \end{array}$$

which is capable of inclusion into the polymeric backbone of the soil release polymers of the present invention as an $-A-R^5-A-$ backbone segment. The units are easily incorporated into the oligomer or polymer backbone by using starting materials having the general formula

$$\begin{array}{l} HO-CH_2-CH-OH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2(OCH_2CH_2)_xSO_3^-\,Na^+ \end{array}$$

wherein x, for the purposes of the L moiety of the present invention, is from 0 to 20.

Other suitable monomers capable of inclusion into the backbone of the type A preferred non-cotton soil release polymers of the present invention as R^5 moieties includes the alkylene poly(oxyalkylene)oxyarylene containing monomer having the general formula



wherein x is 0 to 20. A further example of a preferred monomer resulting in a preferred R^5 unit wherein i is equal to 0, are the sodiosulfopoly(ethyleneoxy)methyl-1,2-propanediols having the formula

$$\begin{array}{l} HO-CH_2-CH-OH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2(OCH_2CH_2)_xSO_3^-Na^+ \end{array}$$

wherein x is from 0 to about 20; more preferred are the monomers

$$\begin{array}{l} HO-CH_2-CH-CH_2-OH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad OCH_2CH_2SO_3^-Na^+ \end{array} \quad \text{or} \quad \begin{array}{l} \qquad\qquad\quad OH \\ \qquad\qquad\quad | \\ HO-CH_2-CH-CH_2 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad OCH_2CH_2SO_3^-Na^+ \end{array}$$

The preferred non-cotton soil release agents of the present invention in addition to the afore-mentioned R^1, R^2, R^3, R^4, and R^5 units also comprise one or more capping groups, -(Cap). The capping groups are independently selected from ethoxylated or propoxylated hydroxyethane and propanesulfonate units of the formula

$(MO_3S)(CH_2)_m(R^{11}O)_n$-, where M is a salt forming cation such as sodium or tetralkylammonium as described herein above, R^{11} is ethylene or propylene or a mixture thereof, m is 0 or 1, and n is from 1 to 20, preferably n is from 1 to about 4; sulfoaroyl units of the formula $-(O)C(C_6H_4)(SO_3^-M^+)$, wherein M is a salt forming cation as described herein above; modified poly(oxyethylene)oxy monoalkyl ether units of the formula $R^{12}O(CH_2CH_2O)_k$- wherein R^{12} contains from 1 to 4 carbon atoms, R^{12} is preferably methyl, and k is from about 3 to about 100, preferably about 3 to about 50, more preferably 3 to about 30; and ethoxylated or propoxylated phenolsulfonate end-capping units of the formula $MO_3S(C_6H_4)(OR^{13})_nO$-, wherein n is from to 20; M is a salt-forming cation; and R^{13} is ethylene, propylene and mixtures thereof.

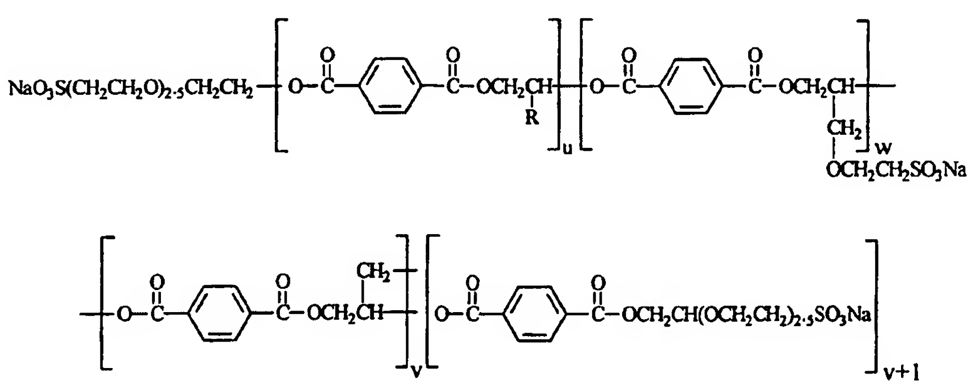
Most preferred end capping unit is the isethionate-type end capping unit which is a hydroxyethane moiety, $(MO_3S)(CH_2)_m(R^{11}O)_n$-, preferably R^{11} is ethyl, m is equal to 0, and n is from 2 to 4.

The value of t is 0 or 1; the value of u is from about 0 to about 60; the value of v is from about 0 to about 35; the value of w is from 0 to 35.

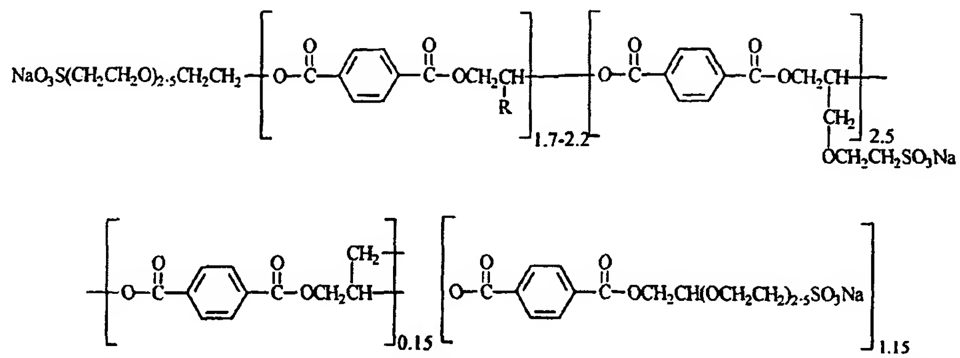
Preferred non-cotton soil release polymers of the present invention having the formula

$$[(Cap)(R^4)_t][(A\text{-}R^1\text{-}A\text{-}R^2)_u(A\text{-}R^1\text{-}A\text{-}R^3)_v(A\text{-}R^1\text{-}A\text{-}R^5)_w\text{-}A\text{-}R^1\text{-}A\text{-}][(R^4)_t(Cap)]$$

can be conveniently expressed as the following generic structural formula



The following structure is an example of the preferred non-cotton soil release polymers of the present invention.



The above-described preferred non-cotton soil release agents are fully described in U.S. Patent Application Serial No. 08/545,351 filed November 22, 1995 which is a continuation-in-part of U.S. Patent Application Serial No. 08/355,938 filed December 14, 1994, both of which are incorporated herein by reference. Other non-cotton soil release polymers suitable for use in the compositions of the present invention are further described herein below.

The preferred non-cotton SRA's can be further described as oligomeric esters comprising: (1) a backbone comprising (a) at least one unit selected from the group consisting of dihydroxysulfonates, polyhydroxy sulfonates, a unit which is at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, and combinations thereof; (b) at least one unit which is a terephthaloyl moiety; and (c) at least one unsulfonated unit which is a 1,2-oxyalkyleneoxy moiety; and (2) one or more capping units selected from nonionic capping units, anionic capping units such as alkoxylated, preferably ethoxylated, isethionates, alkoxylated propanesulfonates, alkoxylated propanedisulfonates, alkoxylated phenolsulfonates, sulfoaroyl derivatives and mixtures thereof. Preferred are esters of the empirical formula:

$$\{(CAP)x(EG/PG)y'(DEG)y''(PEG)y'''(T)z(SIP)z'(SEG)q(B)m\}$$

wherein CAP, EG/PG, PEG, T and SIP are as defined as terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propylene (EG/PG) units, end-caps (CAP), poly(ethyleneglycol) (PEG), (DEG) represents di(oxyethylene)oxy units, (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units, (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, x is from about 1 to about 12, y' is from about 0.5 to about 25, y'' is from 0 to about 12, y''' is from 0 to about 10, y'+y''+y''' totals from about 0.5 to about 25, z is from about 1.5 to about 25, z' is from 0 to about 12; z + z' totals from about 1.5 to about 25, q is from about 0.05 to about 12; m is from about 0.01 to about 10, and x, y', y'', y''', z, z', q and m represent the average number of

moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from about 500 to about 5,000.

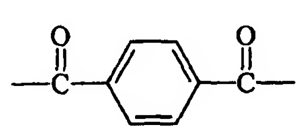
Preferred SEG and CAP monomers for the above esters include Na-2-(2-,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-{2-(2-hydroxyethoxy) ethoxy} ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl alcohol. Preferred SRA esters in this class include the product of transesterifying and oligomerizing sodium 2-{2-(2-hydroxy-ethoxy)ethoxy}ethanesulfonate and/or sodium 2-[2-{2-(2-hydroxyethoxy)ethoxy}-ethoxy]ethanesulfonate, DMT, sodium 2-(2,3-dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)2(T)5(EG/PG)1.4(SEG)2.5(B)0.13 wherein CAP is $(Na+{-}O_3S[CH_2CH_2O]3.5)$- and B is a unit from glycerin and the mole ratio EG/PG is about 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

Preferred non-cotton soil release agent - B. A second preferred class of suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water.

Suitable for use in the laundry detergent compositions of the present invention are preferred non-cotton soil release polymers comprising:

a) one or two terminal units selected from the group consisting of
   i) $-(CH_2)_q(CHSO_3M)CH_2SO_3M$,
   ii) $-(CH_2)_q(CHSO_2M)CH_2SO_3M$,
   iii) $-CH_2CH_2SO_3M$,
   iv) and mixtures thereof; wherein q has the value from 1 to about 4, M is a water soluble cation, preferably sodium;

b) a backbone comprising:
   i) arylene units, preferably terephthalate units having the formula:



;

   ii) ethyleneoxy units having the formula:

$$—O(CH_2CH_2O)_nCH_2CH_2O—$$

wherein the value of n is from about 1 to about 20; and

iii) 1,2-propyleneoxy units having the formula:

$$—O(CH_2CH(CH_3)O)_nCH_2CH(CH_3)O—$$

wherein the value of n is from about 1 to about 20, and wherein further the preferred backbone of this preferred non-cotton soil release polymer has a backbone comprising arylene repeat units which alternate with the ethyleneoxy and 1,2-propyleneoxy units, such that the mole ratio of ethyleneoxy to 1,2-propyleneoxy units is from 0:1 to about 0.9:0.1, preferably from about 0:1 to about 0.4:0.6, more preferably the arylene units alternate with essentially 1,2-propyleneoxy units.

However, other combinations of the above-identified units may be used to form non-cotton soil release polymers suitable for use in the compositions of the present invention. These combinations are more thoroughly described in U.S. Patent 4,968,451, Scheibel et al., issued November 6, 1990 and incorporated herein by reference.

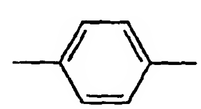
Preferred non-cotton soil release agent - C. Suitable for use in the laundry detergent compositions of the present invention are preferred non-cotton soil release polymers having the formula

$$(Cap)[(A\text{-}R^1\text{-}A\text{-}R^2)_u(A\text{-}R^3\text{-}A\text{-}R^2)_v\text{-}A\text{-}R^4\text{-}A\text{-}](Cap)$$

wherein A is a carboxy linking moiety, preferably A is a carboxy linking moiety having the formula

$$—O—\overset{\displaystyle O}{\overset{\|}{C}}— \quad \text{or} \quad —\overset{\displaystyle O}{\overset{\|}{C}}—O—,$$

R^1 is an arylene moiety, preferably 1,4-phenylene moiety having the formula



wherein for R^1 moieties, the degree of partial substitution with arylene moieties other than 1,4-phenylene should be such that the soil release properties of the compound are not adversely affected to any great extent. Generally, the partial substitution which can be tolerated will depend upon the backbone length of the compound.

R^2 moieties are ethylene moieties or substituted ethylene moieties having C_1-C_4 alkyl or alkoxy substituents. As used herein, the term "the R^2 moieties are essentially ethylene moieties or substituted ethylene moieties having C_1-C_4 alkyl or alkoxy substituents" refers to compounds of the present invention where the R^2 moieties consist entirely of ethylene or substituted ethylene moieties or a partially substituted with other compatible moieties. Examples of these other moieties include 1,3-propylene, 1,4-butylene, 1,5-pentylene, or 1,6-hexylene, 1,2-hydroxyalkylenes and oxyalkylenes.

For the R^2 moieties, the degree of partial substitution with these other moieties should be such that the soil release properties of the compounds are not adversely affected to any great extent. For example, for polyesters made according to the present invention with a 75:25 mole ratio of diethylene glycol ($-CH_2CH_2OCH_2CH_2-$) to ethylene glycol (ethylene) have adequate soil release activity.

For the R^3 moieties, suitable substituted C_2-C_{18} hydrocarbylene moieties can include substituted C_2-C_{12} alkylene, alkenylene, arylene, alkarylene and like moieties, The substituted alkylene or alkenylene moieties can be linear, branched or cyclic. Also, the R^3 can all be the same (e.g. all substituted arylene) or a mixture (e.g. a mixture of substituted arylenes and substituted alkylenes). Preferred R^3 moieties are those which are substituted 1,3-phenylene, preferably 5-sulfo-1,3-phenylene. R^3 moieties are also -A-[(R^2-A-R^4)]-Cap wherein R^4 is R^1, R^3, and mixtures thereof.

The preferred (Cap) moieties comprise units having the formula

$$—[(R^5O)_m(CH_2CH_2O)_n]X$$

wherein R^5 is C_1-C_4 alkylene, or the moiety $-R^2$-A-R^6- wherein R^6 is C_2-C_{12} alkylene, alkenylene, arylene or alkarylene moiety, X is C_1-C_4 alkyl, preferably methyl; the indices m and n are such that the moiety $-CH_2CH_2O-$ comprises at least 50% by weight of the moiety

$$—[(R^5O)_m(CH_2CH_2O)_n]X$$

provided that when R^5 is the moiety $-R^2$-A-R^6-, m is at least 1; each n is at least about 10, the indices u and v are such that the sum of u + v is from about 3 to about 25; the index w is 0 or at least 1; and when w is at least 1, the indices u, v and w have the values such that the sum of u + v + w is from about 3 to about 25.

An example of this type of non-cotton soil release block polyester has the formula

$$X-(OCH_2CH_2)n-(O\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}O-R^2)_u-(O\overset{O}{\overset{\|}{C}}-R^3-\overset{O}{\overset{\|}{C}}O-R^2)_v-O\overset{O}{\overset{\|}{C}}-R^4-\overset{O}{\overset{\|}{C}}O-(CH_2CH_2O)_n\cdot X$$

wherein the R^2 moieties are essentially ethylene moieties, 1,2-propylene moieties, and mixtures thereof; the R^3 moieties are all potassium or preferably sodium 5-sulfo-1,3-phenylene moieties; the R^4 moieties are R^1 or R^3 moieties, or mixtures thereof; each X is ethyl, methyl, preferably methyl; each n is from about 12 to about 43; when w is 0, u + v is from about 3 to about 10; when w is at least 1, u + v + w is from about 3 to about 10.

The above non-cotton soil release polymers of the formula

$$(Cap)[(A\text{-}R^1\text{-}A\text{-}R^2)_u(A\text{-}R^3\text{-}A\text{-}R^2)_v\text{-}A\text{-}R^4\text{-}A\text{-}](Cap)$$

are further described in detail in U.S. Patent 4,702,857, Gosselink, issued October 27, 1987 and incorporated herein by reference.

In addition to the above-described non-cotton soil release polymers, other soil release polymers suitable for use in the liquid laundry detergent compositions of the present invention are further described herein below.

Any other anionic non-cotton soil release agent is suitable for use in the compositions of the present invention alone or in combination except for carboxymethylcellulose (CMC) which cannot be used alone. If the formulator selects CMC for use as an anionic soil release agent in the laundry detergent compositions of the present invention, carboxymethylcellulose must be present in an amount greater than 0.2% by weight, of the composition.

Synthesis of an Oligomer of Sodium 2-[2-(2-Hydroxyethoxy)ethoxy]ethanesulfonate, Dimethyl Terephthalate, Sodium 2-(2,3-Dihydroxypropoxy)ethanesulfonate, Ethylene Glycol, and Propylene Glycol)

To a 250ml, three neck, round bottom flask equipped with a magnetic stirring bar, modified Claisen head, condenser (set for distillation), thermometer, and temperature controller (Therm-O-Watch®, I^2R) is added sodium 2-[2-(2-hydroxyethoxy)ethoxy]ethanesulfonate (7.0g, 0.030 mol), dimethyl terephthalate (14.4g, 0.074 mol), sodium 2-(2,3-dihydroxypropoxy)ethanesulfonate (6.6g, 0.030 mol), ethylene glycol (Baker, 14.0g, 0.225 mol), propylene glycol (Fisher, 18.3g, 0.240 mol), and titanium (IV) propoxide (0.01g, 0.02% of total reaction weight). This mixture is heated to 180°C and maintained at that temperature overnight under argon as methanol distills from the reaction vessel. The material is transferred to a 500ml, single neck, round bottom flask and heated gradually over about 20 minutes to 240°C in a Kugelrohr apparatus (Aldrich) at about 0.1 mm Hg and maintained there for 110 minutes. The reaction flask is then allowed to air cool quite rapidly to near room temperature under

vacuum (~30 min.) The reaction affords 24.4g of the desired oligomer as a brown glass. A ^{13}C-NMR(DMSO-d_6) shows a resonance for -C(O)O$\underline{C}$H2$\underline{C}$H2O(O)C- at ~63.2 ppm (diester) and a resonance for -C(O)O$\underline{C}$H2CH2OH at ~59.4 ppm (monoester). The ratio of the diester peak to monoester peak is measured to be 8. Resonances at ~51.5 ppm and ~51.6 ppm representing the sulfoethoxy groups (-$\underline{C}$H2SO3Na) are also present. A ^{1}H-NMR(DMSO-d_6) shows a resonance at ~7.9 ppm representing terephthalate aromatic hydrogens. Analysis by Hydrolysis-GC shows that the mole ratio of incorporated ethylene glycol to incorporated propylene glycol is 1.6:1. The solubility is tested by weighing a small amount of material into a vial, adding enough distilled water to make a 35% by weight solution, and agitating the vial vigorously. The material is readily soluble under these conditions.

Bleaching Compounds - Bleaching Agents and Bleach Activators - The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

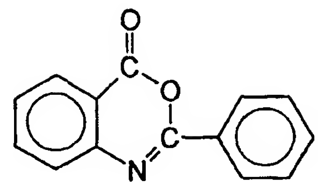
Highly preferred amido-derived bleach activators are those of the formulae:

$$R^1N(R^5)C(O)R^2C(O)L \qquad \text{or} \qquad R^1C(O)N(R^5)R^2C(O)L$$

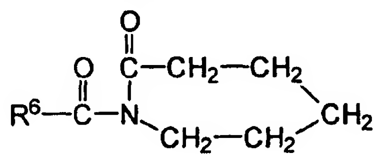
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



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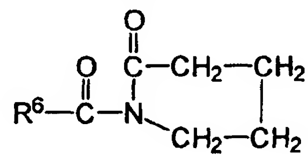


wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2\text{-}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_3$, $Mn^{IV}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})\text{-}(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those

disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Cobalt bleach catalysts useful herein are known, and are described, for example, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]\ T_y$, wherein "OAc" represents an acetate moiety and "T_y" is an anion, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7,1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

As a practical matter, and not by way of limitation, the automatic dishwashing compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic dishwashing process, typical automatic dishwashing compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the cleaning compositions.

Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil

removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. See U.S. Patent 4,891,160, VanderMeer, issued January 2, 1990 and WO 95/32272, published November 30, 1995. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

<u>Brightener</u> - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which

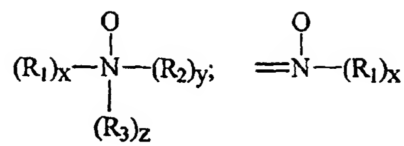
include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naptho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naptho[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R\text{-}A_x\text{-}P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1, R_2, R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

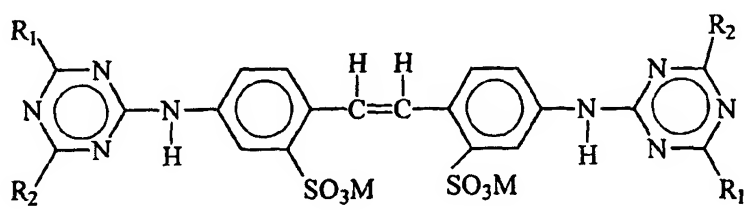
Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to

about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is

commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotri-acetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at lease low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates)

as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

<u>Suds Suppressors</u> - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-

alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

(i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;

(ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(CH_3)_3SiO_{1/2}$ units of SiO_2 units in a ratio of from

$(CH_3)_3\ SiO_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and

(iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone uds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C_6-C_{16} alkyl alcohols having a C_1-C_{16} chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 10% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Alkoxylated Polycarboxylates - Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal

performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-hydroxy-3,7-dimethyl ocatanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal

and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; tricyclodecenyl propionate; tricyclodecenyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; para-tert-butyl cyclohexyl acetate; methyl dihydro jasmonate; beta-napthol methyl ether; methyl beta-naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecenyl acetate; and tricyclodecenyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume compositions.

Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C_{10}-C_{16} alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C_{10}-C_{14} monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, water-soluble magnesium and/or calcium salts such as $MgCl_2$,

$MgSO_4$, $CaCl_2$, $CaSO_4$ and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various detersive ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detersive ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detersive ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detersive function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C_{13-15} ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Liquid dishwashing product formulations preferably have a pH between about 6.8 and about 9.0. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Granules Manufacture

Adding the alkoxylated cationics of this invention into a crutcher mix, followed by conventional spray drying, helps remove any residual, potentially malodorous, short-chain amine contaminants. In the event the formulator wishes to prepare an admixable

particle containing the alkoxylated cationics for use in, for example, a high density granular detergent, it is preferred that the particle composition not be highly alkaline. Processes for preparing high density (above 540 g/l) granules are described in U.S. Patent 5,366,652. Such particles may be formulated to have an effective pH in-use of 9, or below, to avoid the odor of impurity amines. This can be achieved by adding a small amount of acidity source such as boric acid, citric acid, or the like, or an appropriate pH buffer, to the particle. In an alternate mode, the prospective problems associated with amine malodors can be masked by use of perfume ingredients, as disclosed herein.

<u>Liquid Detergents</u>

The manufacture of heavy duty liquid detergent compositions, especially those designed for fabric laundering, which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate detersive ingredients (e.g., bleaching agents, as disclosed hereinabove) stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references. The AQD dispersants are incorporated in the compositions at the levels and in the manner described hereinabove for the manufacture of other laundry detergent compositions.

The compositions of this invention can be used to form aqueous washing solutions for use in the laundering and bleaching of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering/bleaching solutions. The aqueous washing/bleaching solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered and bleached therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering/bleaching solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing/bleaching solution.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

In the following Examples all levels are quoted as % by weight of the composition.

EXAMPLE I

The following liquid detergent compositions are made :

Ingredient	Example a	Example b	Example c
	Wt %	Wt %	Wt%
C12-15alkyl polyethoxylate (1.8) sulfate	21.4	20.2	--
C12-15alkyl polyethoxylate (2.5) sulfate	-	-	19.0
Ethanol	3.7	3.6	3.4
Monoethanolamine	1.0	1.0	1.0
C10 amidopropyldimethyl amine	0.5	0.5	--
Propandiol	6.8	6.4	6.2
C12-13Alkyl polyethoxylate (9)	0.7	0.6	2.0
C12-14 alkyl glucose amide	2.7	2.5	3.5
C12-14 fatty acid	2.0	2.0	2.0
Sodium toluene sulfonate	2.3	2.5	2.5
Citric acid	3.5	3.0	3.0
Borax	2.5	2.5	2.5
Sodium hydroxide (to pH 8.0)	2.5	2.5	3.0
Lipolase (100KLU/g)	0.1	0.08	0.04
Amylase (300KNU/g)	0.2	0.2	0.1
Carezyme (5000cevu/g)	0.05	0.5	0.3
Protease (32g/L)	0.9	0.8	1.0
Soil Release Polymer*	0.2	0.5	0.3
AQD**	1.0	2.0	1.2
Polyethyleneimine, MW 600 ethoxylated (20 moles EO/nitrogen)	1.0	--	--
Water, perfume, enzymes, suds suppressor, brightener & other optional ingredients	to 100%	to 100%	to 100%

* Oligomer of Sodium 2-[2-(2-Hydroxyethoxy)ethoxy]ethanesulfonate, Dimethyl Terephthalate, Sodium 2-(2,3-Dihydroxypropoxy)ethanesulfonate, Ethylene Glycol, and Propylene Glycol) or mixtures of those per U.S. Patent 5,415,807

** 24-ethoxylated quaternized hexamethylenediamine

EXAMPLE II

The following liquid detergent compositions are made :

Ingredient	Example a	Example b	Example c
	Wt %	Wt %	Wt%
C12-15alkyl polyethoxylate (3) sulfate	12.5	21.9	20.0
C12-15 alkyl sulfate	7.7	--	--
Ethanol	5.5	5.5	5.5
Monoethanolamine	to pH 7.8	to pH 7.8	to pH 7.8
C10 amidopropyldimethylamine	1.2	1.2	1.5

Propandiol	8.4	8.5	8.5
C12-13Alkyl polyethoxylate (6.5)	2.5	2.8	2.7
C12-14 alkyl glucose amide	3.8	4.2	4.1
C12-16 fatty acid	4.5	4.5	4.5
Sodium xylene sulfonate	1.9	1.9	1.9
Citric acid	3.0	3.0	3.0
Sodium hydroxide	0.7	0.4	0.9
Protease enzyme (32g/L)	1.5	1.5	1.5
Amylase (300 KNU/g)	0.1	0.4	0.14
Carezyme (5000 cevu/g)	0.8	0.1	0.5
Lipolase Ultra (100 KLU/g)	0.1	0.2	0.15
AQD*	3.0	3.0	2.0
Polyethyleneimine, MW 1200 ethoxylated (7 moles EO/nitrogen)	--	--	1.00
Soil Release Polymer**	0.3	0.3	0.3
Water, perfume, enzymes, fluorscent brightener, stabilizers, suds suppressor & other optional ingredients	to 100%	to 100%	to 100%

* 24-ethoxylated quaternized hexamethylenediamine

** Oligomer of Sodium 2-[2-(2-Hydroxyethoxy)ethoxy]ethanesulfonate, Dimethyl Terephthalate, Sodium 2-(2,3-Dihydroxypropoxy)ethanesulfonate, Ethylene Glycol, and Propylene Glycol)

EXAMPLE III

The following liquid detergent compositions are made :

Ingredient	Example a
	Wt %
C12-15alkyl polyethoxylate (3) sulfate	4.0
C12-15 alkyl sulfate, branched	14.0
Ethanol	2.2
Monoethanolamine	4.5
C8-10 amidopropyldimethylamine	1.3
Propandiol	9.0
C13-15Alkyl polyethoxylate (4.0)	4.5
C12-14 alkyl glucose amide	4.0
C12-16 fatty acid	7.5
Rapeseed fatty acid	3.2
Citric acid	1.0
Sodium hydroxide	2.4
Protease enzyme (34 g/l)	0.6
Duramyl	0.1
Termamyl (300KNU/g)	0.1
Carezyme (5000 Cevu/g)	0.03
Lipolase Ultra (100KLU/g)	0.1
Endolase (3000 cevu/g)	0.2

AQD*	1.3
PEI 600-E20**	1.3
Soil Release Polymer***	0.2
Water, perfume, enzymes, fluorscent brightener, stabilizers, suds suppressor & other optional ingredients	to 100%

** 24-ethoxylated quaternized hexamethylenediamine

** Ethoxylated polyethyleneimine E20 having an average MW of approximately 600

*** Oligomer of Sodium 2-[2-(2-Hydroxyethoxy)ethoxy]ethanesulfonate, Dimethyl Terephthalate, Sodium 2-(2,3-Dihydroxypropoxy)ethanesulfonate, Ethylene Glycol, and Propylene Glycol)

WHAT IS CLAIMED IS:

1. A detergent composition characterizing, or prepared by combining, an effective amount of one or more quaternized polyamine dispersants of the formula:

$$R_1-\overset{A}{\underset{A}{\overset{|}{\underset{|}{N^{\oplus}}}}}-R-\overset{A}{\underset{A}{\overset{|}{\underset{|}{N^{\oplus}}}}}-R_1 \qquad 2X^{\ominus}$$

where R is selected from linear or branched C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, $[(CH_2CH_2O)_qCH_2CH_2]$- and -$CH_2CH(OH)CH_2O$-$(CH_2CH_2O)_qCH_2CH(OH)CH_2]$- where q is from 1 to 100; each R_1 is independently selected from C_1-C_4 alkyl, C_7-C_{12} alkylaryl, or A; A is

$$(\underset{R_3}{\underset{|}{CH}}-CH_2-O)_nB$$

where R_3 is selected from H, C_1-C_3 alkyl, n is from 5 to 100, B is selected from H, C_1-C_4 alkyl, acetyl or benzoyl; and X is a water soluble anion;
said composition further comprising an effective amount of a detersive or fabric care adjunct ingredient which is a member selected from the group consisting of: surfactants; soil release agents; lipase or amylase enzymes; polyethoxyated polyethyleneamine polymers or ethoxylated polyethyleneimine having a MW of less than 1,000; and mixtures thereof.

2. A composition according to Claim 1 wherein R is selected from C_4 to C_8 alkylene, R_1 is selected from C_1-C_2 alkyl, or C_2-C_3 hydroxyalkyl;
A is:

$$(\underset{R_3}{\underset{|}{CH}}-CH_2-O)_nH$$

where R_3 is selected from H or methyl; n is from 10 to 50, and m is 1.

3. A composition according to any preceding claim wherein R is linear or branched C_6; R_1 is methyl; R_3 is H; and n is from 20 to 50.

4. A composition according to any preceding claim in a granular, bar, aqueous liquid or non-aqueous liquid, or tablet form.

5. A composition according to any preceding claim in non-aqueous liquid form and wherein said surfactant is linear alkyl benzene sulfonate.

6. A composition according to any preceding claim in aqueous liquid form and wherein said surfactant is nil linear alkyl benzene sulfonate and comprises alkyl sulfate and alkyl alkoxylated sulfate surfactants.

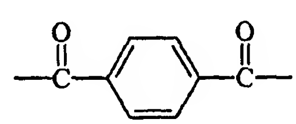
7. A composition according to any preceding claim further comprising amidopropyldimethylamines.

8. A composition according to any preceding claim in granular form and further comprising a polycarboxylate builer.

9. A composition according to any preceding claim comprising a soil release agent which comprises at least 0.01% by weight, of a non-cotton soil release agent selected from the group consisting of a terephthalate co-polymer comprising:

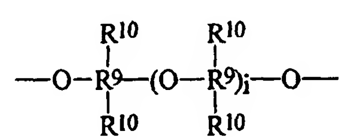
i) a backbone comprising:

a) at least one moiety having the formula:



;

b) at least one moiety having the formula:



wherein R^9 is C_2-C_6 linear alkylene, C_3-C_6 branched alkylene, C_5-C_7 cyclic alkylene, and mixtures thereof; R^{10} is independently selected from hydrogen or -L-SO_3^- M^+; wherein L is a side chain moiety selected from the group consisting of alkylene, oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxy-

alkyleneoxyarylene, poly(oxyalkylene)oxyarlyene, alkylene-poly(oxyalkylene), and mixtures thereof; M is hydrogen or a salt forming cation; i has the value of 0 or 1;

c) at least one trifunctional, ester-forming, branching moiety;

d) at least one 1,2-oxyalkyleneoxy moiety; and

ii) one or more capping units comprising:

a) ethoxylated or propoxylated hydroxyethanesulfonate or ethoxylated or propoxylated hydroxypropanesulfonate units of the formula $(MO_3S)(CH_2)_m(R^{11}O)_n$-, where M is a salt forming cation, R^{11} is ethylene, propylene, and mixtures thereof, m is 0 or 1, and n is from 1 to 20;

b) sulfoaroyl units of the formula $-(O)C(C_6H_4)(SO_3^-M^+)$, wherein M is a salt forming cation;

c) modified poly(oxyethylene)oxy monoalkyl ether units of the formula $R^{12}O(CH_2CH_2O)_k$-, wherein R^{12} contains from 1 to 4 carbon atoms and k is from 3 to 100; and

d) ethoxylated or propoxylated phenolsulfonate end-capping units of the formula $MO_3S(C_6H_4)(OR^{13})_nO$-, wherein n is from 1 to 20; M is a salt-forming cation; and R^{13} is ethylene, propylene, and mixtures thereof;

a sulfonated oligomeric ester composition comprising the sulfonated product of a pre-formed, substantially linear ester oligomer, said linear ester oligomer comprising, per mole,

i) 2 moles of terminal units wherein from 1 mole to 2 moles of said terminal units are derived from an olefinically unsaturated component selected from the group consisting of allyl alcohol and methallyl alcohol, and any remaining of said terminal units are other units of said linear ester oligomer;

ii) from 1 mole to 4 moles of nonionic hydrophile units, said hydrophile units being derived from alkyleneoxides, said alkylene oxides comprising from 50% to 100% ethylene oxide;

iii) from 1.1 moles to 20 moles of repeat units derived from an aryldicarbonyl component wherein said aryldicarbonyl component is comprised of from 50% to 100% dimethylterephthalate, whereby the repeat units derived from said dimethylterephthalate are terephthaloyl; and

iv) from 0.1 moles to 19 moles of repeat units derived from a diol component selected from the group consisting of C_2-C_4 glycols;

wherein the extent of sulfonation of said sulfonated oligomeric ester composition is such that said terminal units are chemically modified by

v) from 1 mole to 4 moles of terminal unit substituent groups of formula $-SO_xM$ wherein x is 2 or 3, said terminal unit substituent groups being derived from a bisulfite component selected from the group consisting of HSO_3M wherein M is a conventional water-soluble cation;

a capped terephalate co-polymer having the formula

$$X[(OCH_2CH_2)_n(OR_5)_m][(A-R^1-A-R^2)_u(A-R^3-A-R^2)_v]— \\ A-R^4-A[(R^5O)_m(CH_2CH_2O)_n]X$$

wherein each of the A moieties is selected from the group consisting of

$$—O\overset{O}{\overset{\|}{C}}— \quad , \quad —\overset{O}{\overset{\|}{C}}O—$$

and combinations thereof, each of the R^1 moieties is selected from the group consisting of 1,4-phenylene and combinations thereof with 1,3-phenylene, 1,2 phenylene, 1,8-naphthylene, 1,4-naphthylene, 2,2'-biphenylene, 4,4'-biphenylene, C_1-C_8 alkylene, C_1-C_8 alkenylene and mixtures thereof the R^2 moieties are each selected from the group consisting of ethylene moieties, substituted ethylene moieties having C_1-C_4 alkyl, alkoxy substitiuents, and mixtures thereof; the R^3 moieties are substituted C_2-C_{18} hydrocarbylene moieties having at least one $-CO_2M$, $-O[(R^5O)_m(CH_2CH_2O)_n]X$ or $-A[(R^2\text{-}A\text{-}R^4\text{-}A)]_w[(R^5O)_m(CH_2CH_2O)_n]X$ substituent; the R^4 moieties are R^1 or R^3 moieties, or mixtures thereof; each R^5 is C_1-C_4 alkylene, or the moiety $-R^2\text{-}A\text{-}R^6\text{-}$ wherein R^6 is a C_1-C_{12} alkylene, alkenylene, arylene, or alkarylene moiety; each M is hydrogen or a water-soluble cation; each X is C_1-C_4 alkyl; the indices m and n have the values such that the moiety $-(CH_2CH_2O)-$ comprises at least 50% by weight of the moiety $[(R^5O)_m(CH_2CH_2O)_n]$, provided that when R^5 is the moiety $-R^2\text{-}A\text{-}R^6\text{-}$, m is 1; each n is at least 10; the indices u and v have the value such that the sum of u + v is from 3 to 25; the index w is 0 or at least 1; and when w is at least 1 u, v and w have the value such that the sum of u + v + w is from 3 to 25; and mixtures thereof.

10. A method for removing soils and stains by contacting said soils and stains with a detergent composition, or aqueous medium comprising said detergent composition, according to any preceding claim.